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# Ionized and excited states of ferrocene: Symmetry adapted cluster–configuration–interaction study

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The ground state, singlet, and triplet excited states, and ionized states of ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$  were studied by the symmetry adapted cluster (SAC)/SAC–configuration–interaction method. The calculated ionization energies and intensities fairly well reproduced the observed photoelectron spectrum in the wide region of 6–14 eV. In particular, the first two peaks ( ${}^2E'_2$  and  ${}^2A'_1$ ) were assigned to the ionizations from the occupied 3*d* orbitals of Fe, mixed already with the two-electron shake-up processes. This is the first *ab initio* quantitative assignment that is consistent with the experimental data. For the singlet states, three *d*–*d* transitions were calculated at 2.12, 2.26, and 4.02 eV, which correspond to the experimental peaks observed at 2.69, 2.97, and 3.82 eV. We propose possible assignments for other absorption bands in the range of 2.12–6.57 eV. In another three triplet *d*–*d* transition states we calculated, we found that the energy order of these states ( $1\ {}^3E''_1$ ,  $1\ {}^3E''_2$ ,  $2\ {}^3E''_1$ ) differs from that of singlet states ( $1\ {}^1E''_2$ ,  $1\ {}^1E''_1$ ,  $2\ {}^1E''_1$ ). © 2002 American Institute of Physics. [DOI: 10.1063/1.1504709]

## I. INTRODUCTION

Since the discovery of ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$ ,<sup>1,2</sup> a number of studies have clarified its structure, reactions, and properties.<sup>3,4</sup> Ultraviolet and visible absorption spectra, in particular, have been studied extensively to clarify the electronic structure of ferrocene in its ground and excited states.<sup>5–11</sup> Photoelectron spectra of various ferrocene-type compounds have also been observed and are well documented.<sup>7–9</sup> Armstrong *et al.*<sup>10</sup> and Sohn *et al.*<sup>11</sup> reported that ferrocene exhibits at least 11 absorption bands in the range of 18 000–53 000  $\text{cm}^{-1}$  (2.2–6.5 eV). Using the ligand-field theory, three *d*–*d* transitions were expected for *d*<sup>6</sup>-ferrocene, though there is considerable ambiguity in the location of these three transitions. Further, the positions of the spin-forbidden *d*–*d* transitions are unclear because of their small intensities. In the ionization spectrum, the first and second peaks were inferred from experimental data to be the ionizations from the 3*d* orbitals.<sup>8,9</sup>

A number of theoretical studies reported the bonding character of the ferrocene ground state.<sup>4</sup> The bonding nature between Fe and two cyclopentadienyl (Cp) rings is reasonably understood as the dative bond between  $\text{Fe}^{2+}$  and  $\text{Cp}^-$ .<sup>3,12</sup> Recently, the mechanism of the protonation of ferrocene in the ground state has been studied using the CCSD(T) method.<sup>13</sup>

For ferrocene ionization energies,  $\Delta\text{SCF}$  calculations,<sup>14,15</sup>  $X\alpha$  scattered-wave calculations,<sup>16,17</sup> and intermediate neglect of differential overlap (INDO) Green's function calculation<sup>18</sup> have been done. Ohno *et al.*<sup>19</sup> calculated the ionization energies with the *ab initio* third-order algebraic diagrammatic construction [ADC(3)] Green's function method and proposed the lowest four peaks to be  $E'_2$  (metal),  $E'_1$  (ligand),  $E''_1$  (ligand), and  $A'_1$  (metal). All calculations have contradicted with the experimental assignment, the

lowest  $E'_2$  (metal) and  $A'_1$  (metal) states, either qualitatively or quantitatively.

For ultraviolet-visible absorption spectra of ferrocene, on the other hand, Rohmer *et al.*<sup>20</sup> proposed a theoretical assignment based on *ab initio* singly excited configuration interaction (SECI) calculations. Zerner *et al.*<sup>21</sup> also proposed a different assignment based on semiempirical INDO–SECI calculations. The calculated results did not satisfactorily agree with the experimental transition energies due to the small basis sets and/or the lack of electron correlations. More reliable *ab initio* studies are necessary to truly understand the electronic structures of the ground, excited, and ionized states of ferrocene.

This paper addresses this subject using the symmetry adapted cluster (SAC)<sup>22</sup> and SAC–configuration–interaction (SAC–CI)<sup>23</sup> methods, which have been applied successfully to the spectroscopies of various molecules<sup>24</sup> including transition metal complexes.<sup>25–27</sup> We assign the photoelectron spectra and the ultraviolet-visible absorption spectra of ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$  by calculating the ground state, singlet, and triplet excited states, and ionized doublet states of this molecule.

## II. METHOD

We used the Gaussian basis functions of triple-zeta quality for Fe and double-zeta quality for C and H; Huzinaga's (533111/52111/311) basis set is used for Fe,<sup>28</sup> Huzinaga's (5121/41) set for C,<sup>28</sup> and Huzinaga–Dunning's (31) set for H.<sup>29</sup> The basis set for Fe was augmented with Hay's flexible *d* function ( $\zeta=0.1133$ )<sup>30</sup> and the augmented double-zeta ANO *f* functions of Roos *et al.*<sup>31</sup> The basis set for C was augmented with a polarization *d* function ( $\zeta=0.6$ )<sup>28</sup> and that of H with a polarization *p* function ( $\zeta=1.0$ ).<sup>29</sup> On the

TABLE I. Orbital energies and orbital characters of some important occupied and unoccupied MOs.

Occupied				Unoccupied			
No.	Symmetry	Orbital energy (eV)	Character	No.	Symmetry	Orbital energy (eV)	Character
47,48	$4e_1''$	-9.11	$\text{Cp}(\pi) + \text{Fe}(d_{xz}, d_{yz})$	49	$9a_1'$	0.29	$\text{Fe}(s) + \text{Cp}(\text{Ryd}(s, d_{z2}))$
45,46	$6e_1'$	-9.25	$\text{Cp}(\pi) + \text{Fe}(p_x, p_y)$	50	$7a_2''$	0.44	$\text{Fe}(p_z) + \text{Cp}(\text{Ryd}(s, p_z, d_{z2}))$
43,44	$4e_2'$	-11.44	$\text{Fe}(d_{xy}, d_{x2-y2})$	51,52	$5e_1''$	0.79	$\text{Fe}(d_{xz}, d_{yz}) + \text{Cp}(\text{Ryd}(p_x, p_y))$
42	$6a_2''$	-13.31	$\text{Cp}(\pi) + \text{Fe}(p_z)$	53	$10a_1'$	0.80	$\text{Fe}(s) + \text{Cp}(\text{Ryd}(s, d_{z2}))$
41	$8a_1'$	-13.82	$\text{Fe}(d_{z2}, s)$	56,57	$7e_1'$	0.94	$\text{Fe}(p_x, p_y) + \text{Cp}(\text{Ryd}(p_x, p_y))$
39,40	$3e_2''$	-14.04	$\text{Cp}(\sigma)$	63	$11a_1'$	1.31	$\text{Fe}(s) + \text{Cp}(\text{Ryd}(s, p_z, d_{z2}))$
37,38	$3e_2'$	-14.30	$\text{Cp}(\sigma)$	64	$9a_2''$	1.49	$\text{Fe}(p_z) + \text{Cp}(\text{Ryd}(s, p_z, d_{z2}))$
35,36	$5e_1'$	-14.95	$\text{Cp}(\sigma)$	65	$12a_1'$	2.03	$\text{Fe}(s) + \text{Cp}(\text{Ryd}(s, p_z, d_{z2}))$
33,34	$3e_1''$	-15.10	$\text{Cp}(\sigma)$	66,67	$6e_1''$	2.14	$\text{Fe}(d_{xz}, d_{yz}) + \text{Cp}(\text{Ryd}(p_x, p_y))$
32	$7a_1'$	-15.24	$\text{Cp}(\pi)$	78,79	$7e_1'$	3.90	$\text{Fe}(d_{xz}, d_{yz}) + \text{Cp}(\text{Ryd}(p_x, p_y))$
				83,84	$7e_2'$	5.28	$\text{Cp}(\pi^*) + \text{Fe}(d_{xy}, d_{x2-y2})$
				86,87	$8e_1''$	6.18	$\text{Cp}(\pi + \text{Ryd}(p_x, p_y)) + \text{Fe}(d_{xz}, d_{yz})$
				92,93	$9e_1''$	7.43	$\text{Fe}(d_{xz}, d_{yz}) + \text{Cp}(\pi + \text{Ryd}(p_x, p_y))$

center of each Cp ring, the  $s$ ,  $p$ , and  $d$  Rydberg functions were added in double-zeta quality.<sup>32</sup> The total number of basis functions is 315.

Experimental geometrical parameters of  $\text{Fe}(\text{C}_5\text{H}_5)_2$  for the ground state are used throughout the present calculations: 2.064 Å for Fe–C, 1.440 Å for C–C in the Cp ring, and 1.104 Å for C–H.<sup>33</sup> The Cp ring is assumed to be planar and the two Cp rings are in an eclipsed conformation ( $D_{5h}$ ), as observed in a gas phase.<sup>34</sup> The  $z$ -axis is defined to be parallel to the Cp–Fe–Cp axis.

The Hartree–Fock (HF) calculations were carried out using the GAUSSIAN 98 program.<sup>35</sup> The electron correlation in the ground state was taken into account by the SAC theory, and those in the singlet and triplet excited states and ionized doublet states by the SAC–CI theory. The active space in SAC and SAC–CI calculations involves 285 HF orbitals; the  $1s$ ,  $2s$ , and  $2p$  orbitals of Fe and  $1s$  orbital of C were treated as frozen-core orbitals. To reduce the configuration number, perturbation selection technique<sup>36</sup> is used with energy thresholds of  $1.0 \times 10^{-5}$  for the ground state,  $1.0 \times 10^{-6}$  for the doublet ionized state, and  $2.0 \times 10^{-6}$  for singlet and triplet excited states.

### III. GROUND STATE

The bonding nature of the ground state of ferrocene has been well documented as described above. Table I summarizes the energies and their characters of some important occupied and unoccupied orbital obtained by the present Hartree–Fock calculation. The highest occupied molecular orbital (homo)  $4e_1''$  and the next homo  $6e_1'$  are essentially the  $\pi$  orbitals of the Cp rings ( $\text{Cp}-\pi$ ) and have small components of the  $3d_{xz}$  and  $3d_{yz}$  or  $4p_x$  and  $4p_y$  orbitals of Fe. We may consider that ferrocene has dative bonds between  $\text{Fe}^{2+}$  and  $\text{Cp}^-$ , electron donation being from  $\text{Cp}^-$  to  $\text{Fe}^{2+}$  through these orbitals. Occupied  $3d$  orbitals of Fe ( $4e_2'$  and  $8a_1'$ ) are lower in energy than the  $\text{Cp}-\pi$  orbitals ( $4e_1''$  and  $6e_1'$ ). The  $4e_2'$  orbitals are essentially the  $3d_{xy}$  and  $3d_{x2-y2}$  atomic orbitals of Fe with a small  $\text{Cp}-\pi$  character, while the  $8a_1'$  orbital has  $3d_{z2}$  and  $4s$  character of Fe. The unoccupied  $3d_{xz}$  and  $3d_{yz}$  orbitals appear as  $9e_1''$ . Therefore, in a simple

ligand-field picture, three singly excited  $d-d$  transitions are expected in this electronic configuration. The total energy at the HF level was  $-1646.4843$  hartree and the ground state correlation energy obtained by the SAC method was  $-0.8361$  hartree.

### IV. IONIZED DOUBLET STATES

Figure 1 shows the calculated SAC–CI ionization energies compared to the observed spectrum,<sup>9</sup> together with the HF orbital energies shown as Koopmans ionization energies. The observed spectrum in Fig. 1 has three bands below 16 eV. First and second bands have two peaks, and the third one has several peaks. The present SAC–CI result satisfactorily reproduces the observed first two bands including four ionized states. The SAC–CI method predicts the third band to have six electronic states. The ionization energies calculated by the SAC–CI method agree well with the observed ones.

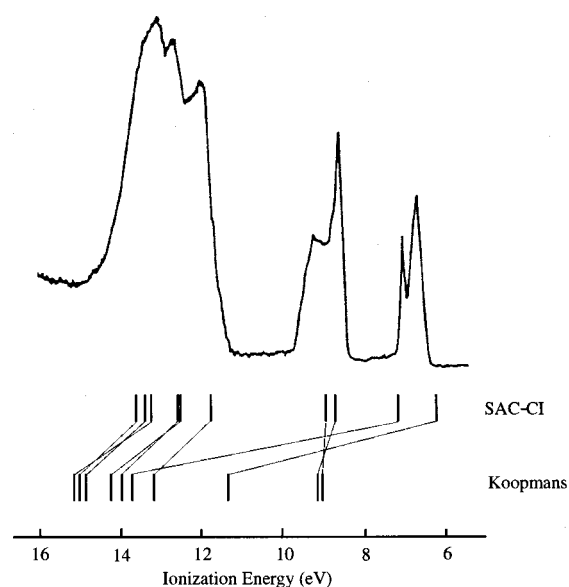


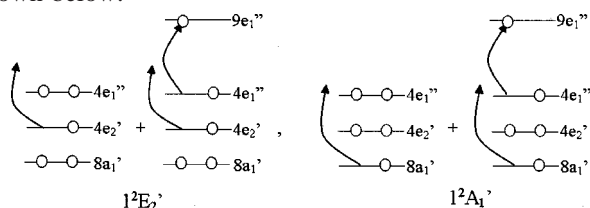
FIG. 1. SAC–CI and Koopmans ionization energies in comparison with the experimental photoelectron spectrum (Ref. 9) of ferrocene.

TABLE II. Ionized doublet states and ionization energies (eV) of ferrocene obtained by SAC–CI, ADC(3), Hartree–Fock, and experiment.

State	Main configurations	SAC–CI <sup>a</sup>	ADC(3) <sup>b</sup>	Koopmans <sup>c</sup>	Expt.
$1^2E'_2$	$0.85(4e'_2) + 0.39(4e''_1, 4e'_2 \rightarrow 9e''_1)$	6.26(1.494)	7.85	11.44	6.86 <sup>d</sup> , 6.88 <sup>e</sup>
$1^2A'_1$	$0.82(8a'_1) + 0.41(4e'_1, 8a'_1 \rightarrow 9e''_1)$	7.27(0.747)	9.36	13.82	7.23 <sup>d,e</sup>
$1^2E'_1$	$6e'_1$	8.78(1.917)	8.70	9.25	8.72 <sup>d,e</sup> , 8.87 <sup>e</sup>
$1^2E''_1$	$4e''_1$	9.05(1.919)	9.08	9.11	9.14 <sup>e</sup> , 9.38 <sup>d</sup> , 9.39 <sup>e</sup>
$1^2A''_2$	$6a''_2$	11.86(0.919)	12.13	13.31	12.2 <sup>d</sup> , 12.3 <sup>e</sup>
$2^2E'_2$	$3e'_2$	12.63(1.910)	13.08	14.30	13.0 <sup>e</sup> , 13.6 <sup>d</sup>
$1^2E''_2$	$3e''_2$	12.65(1.887)	12.96	14.04	13.0 <sup>e</sup> , 13.6 <sup>d</sup>
$2^2A'_1$	$7a'_1$	13.34(0.920)	13.71	15.24	13.46 <sup>e</sup> , 13.6 <sup>d</sup>
$2^2E'_1$	$5e'_1$	13.46(1.956)	13.89	14.95	13.46 <sup>e</sup> , 13.6 <sup>d</sup>
$2^2E''_1$	$3e''_1$	13.69(1.916)	14.07	15.10	13.46 <sup>e</sup> , 13.6 <sup>d</sup>

<sup>a</sup>Values in parentheses indicate intensities.<sup>b</sup>Reference 19.<sup>c</sup>Our work.<sup>d</sup>Reference 8.<sup>e</sup>Reference 9.

Table II lists the ionization energies and the intensities (in parentheses) calculated by the SAC–CI method and the HF method (Koopmans). The ionization energies calculated by the *ab initio* ADC(3) Green's function method<sup>19</sup> and those observed<sup>8,9</sup> are also shown for comparison. The first peak observed at 6.86 eV was calculated at 6.26 eV ( $1^2E'_2$ ) as the ionization mainly from  $4e'_2$  MO. The second peak observed at 7.23 eV was calculated at 7.27 eV ( $1^2A'_1$ ) as the ionization from  $8a'_1$  MO. These states have significant components of two-electron shake-up processes, which are from  $4e''_1$ ,  $4e'_2$  to  $9e''_1$ , and from  $4e''_1$ ,  $8a'_1$  to  $9e''_1$ , respectively, as shown below:



The extents of mixing of these shake-up configurations are very large as seen from the main configuration shown in Table II. It is very remarkable that even the first ionization peak already has a strong mixing of the shake-up ionizations. It is for this reason that the calculated ionization energy differs by more than 0.5 eV from the experimental value.

The next band at around 9 eV is assigned to be composed of the two peaks of the ionizations from the  $\pi$  orbitals of the Cp rings and the  $d$  or  $p$  orbital of Fe. The third peak observed at 8.72 or 8.87 eV was calculated at 8.78 eV ( $1^2E'_1$ ), which is the ionization from the  $6e'_1$  MO. The fourth peak observed at 9.14–9.39 eV was calculated at 9.05 eV ( $1^2E''_1$ ), which is the ionization from  $4e''_1$ . These two peaks do not have the shake-up mixing. The present assignment of the lowest four peaks agrees with the experimental prediction, though these peaks have not been reproduced quantitatively or even qualitatively in the previous theoretical calculations.<sup>14–19</sup> The assignment of the ADC(3) Green's function method differs from ours because the first and second peaks by ADC(3) were not caused by the ionizations from the Fe  $d$  orbitals. The Koopmans picture completely breaks down as seen from Fig. 1; it fails to describe the

ionizations from the  $d$  orbitals of Fe, due to the strong orbital relaxation and/or large electron correlation effects. This is seen from the main configurations of the  $1^2E'_2$  and  $1^2A'_1$  ionized doublet states shown in Table III.

For the next broad band in 11–14 eV, six ionized states were calculated by the SAC–CI method. The fifth peak calculated at 11.86 eV corresponds to the peak observed at 12.2–12.3 eV and originates from the  $\pi$  orbitals of the Cp rings mixed with the  $p$  orbital of Fe. The next higher two pairs of peaks calculated at 12.63, 12.65, and 13.46, 13.69 eV originate from the  $\sigma$  orbitals of the Cp rings, and the peak at 13.34 eV, which lies median between these two pairs of peaks, is the ionization from the  $\pi$  orbital of the Cp rings. Note that the ordering of these six ionized states is quite different from that of the Koopmans picture, as seen from Fig. 1 and from the comparison between Tables I and II. Electron correlations are certainly very important for describing the electronic structures of the ionized states of ferrocene.

## V. SINGLET EXCITED STATES

Table III shows the singlet transition energies and the corresponding main configurations calculated by the SAC–CI method. The results calculated by the *ab initio* SECI method reported by Rohrer *et al.*,<sup>20</sup> and by the INDO–SECI method reported by Zerner *et al.*,<sup>21</sup> and the experimental transition energies<sup>10,11</sup> are also shown in the same table. As for the experimental values, those observed in vapor phase<sup>10,11</sup> and in a solution<sup>10</sup> are shown, since they are complementary with each other.

As expected from the ground-state electronic configuration, three  $d$ – $d$  transitions may appear in the low-lying singlet excited states of ferrocene. The present work certainly gave the lowest three states,  $1^1E'_2$  (2.11 eV),  $1^1E''_1$  (2.27 eV), and  $2^1E'_1$  (4.03 eV), to be essentially the  $d$ – $d$  transitions in character, as expected. However, this energy ordering ( $1^1E'_2$ ,  $1^1E''_1$ ,  $2^1E'_1$ ) is different from that given by the INDO–SECI method ( $1^1E'_1$ ,  $1^1E'_2$ ,  $2^1E'_1$ ).<sup>21</sup> These transitions are dipole-forbidden, so that the observed peaks are very weak. In fact, the lowest two singlet transitions were

TABLE III. Singlet excited states and their excitation energies of ferrocene (eV) obtained by SAC–CI, SECI, INDO–SECI, and experiment.

State	Main configurations	SAC–CI (eV)	SECI <sup>a</sup>	INDO–SECI <sup>b</sup>	Expt. (eV)
1 <sup>1</sup> E'' <sub>2</sub>	4e' <sub>2</sub> →9e'' <sub>1</sub>	2.11	2.63	2.96	2.8 <sup>c</sup> , 2.70 <sup>d</sup>
1 <sup>1</sup> E'' <sub>1</sub>	0.58(4e' <sub>2</sub> →9e'' <sub>1</sub> )–0.54(8a' <sub>1</sub> →9e'' <sub>1</sub> )	2.27	3.31	2.69	2.81 <sup>c</sup> , 2.98 <sup>d</sup>
2 <sup>1</sup> E'' <sub>1</sub>	0.57(8a' <sub>1</sub> →9e'' <sub>1</sub> ) + 0.54(4e' <sub>2</sub> →9e'' <sub>1</sub> )	4.03	5.74	3.96	3.8 <sup>c,d</sup>
			9.05	4.58, 4.92, 4.95	4.67 <sup>c,d</sup>
1 <sup>1</sup> A' <sub>2</sub>	4e'' <sub>1</sub> 9e'' <sub>1</sub>	5.25		5.11	5.02 <sup>c</sup>
1 <sup>1</sup> A' <sub>1</sub>	4e'' <sub>1</sub> 9e'' <sub>1</sub>	5.29		5.26, 5.32, 5.54	5.23 <sup>c</sup>
1 <sup>1</sup> E' <sub>2</sub>	4e'' <sub>1</sub> 9e'' <sub>1</sub>	5.48			
2 <sup>1</sup> A' <sub>2</sub>	4e'' <sub>1</sub> 7e' <sub>2</sub>	5.60	10.17	5.62, 5.69, 5.91	5.82 <sup>c</sup>
				6.22	6.16 <sup>c</sup>
1 <sup>1</sup> E' <sub>1</sub>	0.69(6e' <sub>1</sub> →9a' <sub>1</sub> ) + 0.53(6e' <sub>1</sub> →11a' <sub>1</sub> )	6.34	10.39	6.24	6.20 <sup>d</sup> , 6.31 <sup>c</sup>
2 <sup>1</sup> E' <sub>1</sub>	6e' <sub>1</sub> →9a' <sub>1</sub>	6.43		6.48	6.58 <sup>c</sup>
1 <sup>1</sup> A'' <sub>1</sub>	6e' <sub>1</sub> →9e'' <sub>1</sub>	6.45		7.04	
1 <sup>1</sup> A'' <sub>2</sub>	6e' <sub>1</sub> →9e'' <sub>1</sub>	6.47			
2 <sup>1</sup> A'' <sub>2</sub>	6e' <sub>1</sub> →9e'' <sub>1</sub>	6.56			

<sup>a</sup>Reference 20.<sup>b</sup>Reference 21.<sup>c</sup>Reference 10.<sup>d</sup>Reference 11.

observed at 2.70 and 2.98 eV in solution, but observed as one peak at 2.81 eV in a vapor phase. The next three states calculated by the SAC–CI method are 1 <sup>1</sup>A'<sub>2</sub> (5.25 eV), 1 <sup>1</sup>A'<sub>1</sub> (5.29 eV), and 1 <sup>1</sup>E'<sub>2</sub> (5.48 eV), which are the transitions from Cp–π to 3d<sub>xz</sub>, 3d<sub>xz</sub> of Fe. The experimental values are 5.02 and 5.23 eV. The next state is 2 <sup>1</sup>A'<sub>2</sub> calculated at 5.60 eV in comparison with the experimental value of 5.82 eV, and this is the π–π\* transition of the Cp ring. These transitions are dipole-forbidden and therefore, their experimental peaks have only small intensities, but they are reasonably well reproduced by the present SAC–CI calculations.

The first dipole-allowed transition is the 1 <sup>1</sup>E'<sub>1</sub> state that is calculated at 6.34 eV by the SAC–CI method; the calculated energy well reproduces the observed ones, 6.31 eV in vapor and 6.20 eV in solution. The second dipole-allowed state is 2 <sup>1</sup>E''<sub>1</sub> state calculated at 6.43 eV, which is assigned to the experimental peak observed at 6.58 eV. Thus, the dipole-allowed transitions in this energy region are also well reproduced by the present SAC–CI calculations.

## VI. TRIPLET EXCITED STATES

Table IV displays three triplet *d*–*d* transition energies calculated by the SAC–CI, SECI,<sup>20</sup> and INDO–SECI<sup>21</sup> methods. The SAC–CI main configurations and their coefficients

TABLE IV. Triplet *d*–*d* excitation energies of ferrocene (eV) obtained by SAC–CI, SECI, INDO–SECI, and experiment.

State	Main configurations	SAC–CI (eV)	SECI <sup>a</sup>	INDO–SECI <sup>b</sup>	Expt. (eV) <sup>c</sup>
1 <sup>3</sup> E'' <sub>1</sub>	0.72(4e' <sub>2</sub> →9e'' <sub>1</sub> ) –0.33(8a' <sub>1</sub> →9e'' <sub>1</sub> )	1.40	1.81–1.87	2.54	1.74
1 <sup>3</sup> E'' <sub>2</sub>	4e' <sub>2</sub> →9e'' <sub>1</sub>	1.68	1.81–1.87	2.55	2.05
2 <sup>3</sup> E'' <sub>1</sub>	0.70(8a' <sub>1</sub> →9e'' <sub>1</sub> ) +0.32(8a' <sub>1</sub> →8e'' <sub>1</sub> )	2.60	4.56	2.55	2.29

<sup>a</sup>Reference 20.<sup>b</sup>Reference 21.<sup>c</sup>Reference 10.

are also listed along with the observed excitation energies,<sup>10</sup> which were assigned experimentally to be spin-forbidden transitions. The present SAC–CI calculations indicate that the lowest three triplet excitations are *d*–*d* transitions in nature, as expected similarly from the case of the singlet excitations. The 1 <sup>3</sup>E''<sub>1</sub> is located lower by 0.87 eV than the corresponding singlet 1 <sup>1</sup>E''<sub>1</sub> state, while 1 <sup>3</sup>E''<sub>2</sub> and 2 <sup>3</sup>E''<sub>1</sub> states are lower by 0.43 and 1.43 eV than the corresponding 1 <sup>1</sup>E''<sub>2</sub> and 2 <sup>1</sup>E''<sub>1</sub> states. The large splitting of the singlet and triplet 2E''<sub>1</sub> states implies a considerable mixing of the Cp–π states to the *d* states in the triplet state 2 <sup>3</sup>E''<sub>1</sub>. Thus, the <sup>3</sup>E''<sub>1</sub> state has the lowest energy of these triplet states and the energy ordering of the triplet states (1 <sup>3</sup>E''<sub>1</sub>, 1 <sup>3</sup>E''<sub>2</sub>, 2 <sup>3</sup>E''<sub>1</sub>) is different from that of the singlet states (1 <sup>1</sup>E''<sub>2</sub>, 1 <sup>1</sup>E''<sub>1</sub>, 2 <sup>1</sup>E''<sub>1</sub>). The total energy order, including both singlet and triplet states, is 1 <sup>3</sup>E''<sub>1</sub>, 1 <sup>3</sup>E''<sub>2</sub>, 1 <sup>1</sup>E''<sub>2</sub>, 1 <sup>1</sup>E''<sub>1</sub>, 2 <sup>3</sup>E''<sub>1</sub>, and 2 <sup>1</sup>E''<sub>1</sub>. We assign the calculated 2 <sup>3</sup>E''<sub>1</sub> state (2.60 eV) to the observed peak of 2.29 eV considering its weak intensity and the spin-forbidden nature experimentally suggested, though the calculated 1 <sup>1</sup>E''<sub>2</sub> state (2.11 eV in Table IV) is closer to the 2.29 eV peak than the 2 <sup>3</sup>E''<sub>1</sub> state.

## VII. CONCLUDING REMARKS

This paper summarizes the SAC/SAC–CI study on the ground state, singlet and triplet excited states, and doublet ionized states of ferrocene, Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>. The main results of this paper are as follows:

(1) The ionization spectrum in 6–12 eV energy region is reproduced reasonably by the present calculations. The first and second peaks are assigned to the ionization from occupied 3*d* orbitals of Fe. This assignment is consistent with the experimental one. A remarkable point is the strong mixing of the shake-up processes *even to these lowest ionization states*, showing a break-down of the Koopmans picture.

(2) The second and third broad bands in the ionization spectrum experimentally observed are composed of the two



and six ionized states and were reproduced satisfactorily by the SAC–CI method. The Koopmans ordering was wrong for these states.

(3) The observed peaks at 2.70, 2.98, and 3.82 eV were assigned to the singlet  $d$ – $d$  transitions calculated at 2.11, 2.27, and 4.03 eV. Other dipole-forbidden states were also assigned satisfactorily to the weak peaks experimentally observed.

(4) The absorption observed at 6.31 eV with strong intensity is assigned to the first dipole-allowed  $^1E'_1$  state, whose calculated energy is 6.34 eV. This agreement is much improved over those in the previous works. The second strong absorption peak is also well reproduced and assigned to the second  $^1E'_1$  state.

(5) Three triplet  $d$ – $d$  transition energies are calculated; they well reproduced the three weak peaks observed in 1.74 – 2.29 eV.

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- <sup>1</sup>T. J. Kealy and P. L. Paulson, *Nature* (London) **168**, 1039 (1951).
- <sup>2</sup>S. A. Miller, J. A. Tebbboth, and J. F. Tremaine, *J. Chem. Soc.* **1952**, 632.
- <sup>3</sup>A. Veillard and J. Demuynck, in *Modern Theoretical Chemistry*, edited by H. F. Schaefer III (Plenum, New York, 1997), Vol. 4.
- <sup>4</sup>A. Haaland, *Acc. Chem. Res.* **11**, 415 (1979), and references therein.
- <sup>5</sup>D. R. Scott and R. S. Becker, *J. Chem. Phys.* **35**, 516 (1961).
- <sup>6</sup>J. J. Smith and B. Meyer, *J. Chem. Phys.* **48**, 5436 (1968).
- <sup>7</sup>J. C. Green, *Struct. Bonding* (Berlin) **43**, 37 (1981).
- <sup>8</sup>J. W. Rabalais, L. O. Werme, T. Bergmark, L. Karlsson, M. Hussain, and K. Siegbahn, *J. Chem. Phys.* **57**, 1185 (1972).
- <sup>9</sup>S. Evans, M. L. H. Green, B. Jewitt, A. F. Orchard, and C. F. Pygall, *J. Chem. Soc., Faraday Trans. 2* **68**, 1847 (1972).
- <sup>10</sup>A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.* **46**, 4321 (1967).
- <sup>11</sup>Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Am. Chem. Soc.* **93**, 3603 (1971).
- <sup>12</sup>J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.* **98**, 1729 (1976).
- <sup>13</sup>M. J. Mayor-Lopez, H. P. Lüthi, H. Koch, P. Y. Morgantini, and J. Weber, *J. Chem. Phys.* **113**, 8009 (2000).
- <sup>14</sup>M.-M. Coutiere, J. Demuynck, and A. Veillard, *Theor. Chim. Acta* **27**, 281 (1972).
- <sup>15</sup>P. S. Bagus, U. I. Walgren, and J. Almlöf, *J. Chem. Phys.* **64**, 2324 (1976).
- <sup>16</sup>E. J. Baerends and P. Ross, *Chem. Phys. Lett.* **23**, 391 (1973).
- <sup>17</sup>N. Rösch and K. H. Johnson, *Chem. Phys. Lett.* **24**, 179 (1974).
- <sup>18</sup>M. C. Böhm, *Z. Naturforsch. A* **37A**, 1193 (1982).
- <sup>19</sup>M. Ohno, W. von Niessen, and J. Schüle, *Chem. Phys.* **158**, 1 (1991).
- <sup>20</sup>M.-M. Rohmer, A. Veillard, and M. H. Wood, *Chem. Phys. Lett.* **29**, 466 (1974).
- <sup>21</sup>M. C. Zerner, G. H. Loew, R. F. Kirchner, and U. T. Mueller-Westerhoff, *J. Am. Chem. Soc.* **102**, 589 (1980).
- <sup>22</sup>H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).
- <sup>23</sup>H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978); **67**, 329 (1979); **67**, 334, (1979).
- <sup>24</sup>H. Nakatsuji, *Acta Chim. Hung.* **129**, 719 (1992).
- <sup>25</sup>H. Nakatsuji, J. Hasegawa, and M. Hada, *J. Chem. Phys.* **104**, 2321 (1996); K. Toyota, J. Hasegawa, and H. Nakatsuji, *J. Phys. Chem. A* **101**, 446 (1997); M. Hada, Y. Imai, M. Hidaka, and H. Nakatsuji, *J. Chem. Phys.* **103**, 6993 (1995).
- <sup>26</sup>H. Nakai, Y. Ohmori, and H. Nakatsuji, *J. Chem. Phys.* **95**, 8287 (1991); H. Nakatsuji, M. Ehara, M. H. Palmer, and M. F. Guest, *ibid.* **97**, 2561 (1992); K. Yasuda and H. Nakatsuji, *ibid.* **99**, 1945 (1993); H. Nakai and H. Nakatsuji, *J. Mol. Struct.: THEOCHEM* **331**, 141 (1994).
- <sup>27</sup>S. Jitsuhiro, H. Nakai, M. Hada, and H. Nakatsuji, *J. Chem. Phys.* **101**, 1029 (1994); H. Nakatsuji and M. Ehara, *ibid.* **101**, 7658 (1994).
- <sup>28</sup>S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).
- <sup>29</sup>T. H. Dunning, Jr., *J. Chem. Phys.* **53**, 2823 (1970).
- <sup>30</sup>P. J. Hay, *J. Chem. Phys.* **66**, 4377 (1977).
- <sup>31</sup>R. Pou-Amerigo, M. Merchán, I. Nebot-Gil, P. O. Widmark, and B. Roos, *Theor. Chim. Acta* **92**, 149 (1995).
- <sup>32</sup>H. F. Schaefer III, *Methods of Electronic Structure Theory* (Plenum, New York and London).
- <sup>33</sup>R. K. Bohn and A. Haaland, *J. Organomet. Chem.* **5**, 2653 (1968); A. Haaland and J. E. Nilsson, *Acta Chem. Scand.* (1947–1973) **22**, 2653 (1968); A. Haaland, J. Lusztyk, D. P. Novak, J. Brunvoll, and K. B. Starowieyski, *J. Chem. Soc. Chem. Commun.* **1974**, 54 (1974).
- <sup>34</sup>M. Orsenblum, *Chemistry of Iron Group Metallocenes* (Interscience, New York, 1965), Chap. 3, Part I.
- <sup>35</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.8, Gaussian, Inc., Pittsburgh, PA, 1998.
- <sup>36</sup>H. Nakatsuji, *Chem. Phys.* **75**, 425 (1983).